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Sections of CDA 706 piping and Monel 400 tubing were severely pitted after exposure to marine and estuarine waters, respectively. Surfaces of both alloys were uniformly covered with thick surface deposits, ranging in color from blue-green to reddish brown to black. Pits developed under surface deposits containing 10^4-10^5 sulfate-reducing bacteria (SRB) in association with other bacteria. Pits were irregular in shape, lacking a consistent morphology. The observed corrosion was attributed to a combination of differential aeration cells, a large cathode::small anode surface area, concentration of chlorides, development of acidity within the pits, and the specific reactions of the base metals with sulfides produced by the SRB. Chlorine and sulfur appear to have reacted selectively with iron and nickel in the alloys. Nickel has been selectively removed from pitted areas leaving a copper rich spongy pit interior.
SRB isolated from in-service failures were used to inoculate copper-containing foils in an attempt to identify mineralogical fingerprints that could be used as diagnostic for SRB influenced corrosion of copper alloys. The thickness and tenacity of the resulting sulfide deposits varied among the metals and cultures. Strongly adherent corrosion products contained major amounts of djurleite ($Cu_{1.96}S$). Chalcocite (Cu_2S) as well as traces of covellite (CuS) and digenite (Cu_9S_5) were also identified. Djurleite and the high temperature polymorph of chalcocite may be mineralogical fingerprints for the SRB influenced corrosion of copper-containing metals.

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UNITED STATES NAVY

MISSION ENHANCEMENT THROUGH MATERIAL ENGINEERING

SHIPBOARD CORROSION CONTROL

COHOSTS:

Naval Research Laboratory
• Marine Corrosion Facility •

Naval Sea Systems Command
• Corrosion Control Branch •

29 – 31 October, 1990

Key West, Florida

Microbiologically Influenced Corrosion in Copper and Nickel Seawater Piping Systems

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Executive Summary

Sections of CDA 706 piping and Monel 400 tubing were severely pitted after exposure to marine and estuarine waters, respectively. Surfaces of both alloys were uniformly covered with thick surface deposits, ranging in color from blue-green to reddish brown to black. Pits developed under surface deposits containing 10^4-10^5 sulfate-reducing bacteria (SRB) in association with other bacteria. Pits were irregular in shape, lacking a consistent morphology. The observed corrosion was attributed to a combination of differential aeration cells, a large cathode::small anode surface area, concentration of chlorides, development of acidity within the pits, and the specific reactions of the base metals with sulfides produced by the SRB. Chlorine and sulfur appear to have reacted selectively with iron and nickel in the alloys. Nickel had been selectively removed from pitted areas leaving a copper-rich spongy pit interior.

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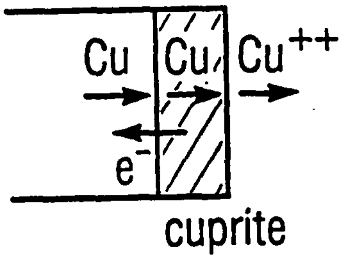
ANODIC SITES



Primary Oxide-Forming Reactions

$4\,Cu + O_2\ (\text{adsorbed}) \rightarrow 2\,Cu_2O\ (\text{cuprite})$

$2\,Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$

Primary Oxidation Reactions for Cu_2O - Covered Metal

$Cu \rightarrow Cu^{++}(aq) + 2e^-$

Follow-Up Reactions

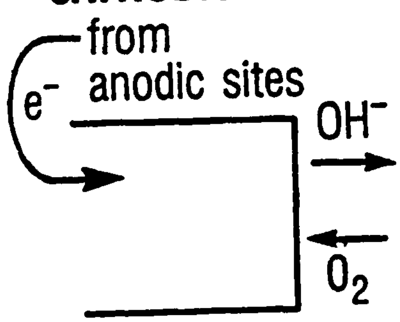
In Seawater:

$2\,Cu^{++} + 3\,OH^- + Cl^- \rightarrow Cu\,(OH)_3Cl\downarrow$

In Fresh Water:

$2\,Cu^{++} + HCO_3^- + 2\,OH^- \rightarrow Cu_2CO_3(OH)_2\downarrow + H^+$

CATHODIC SITES



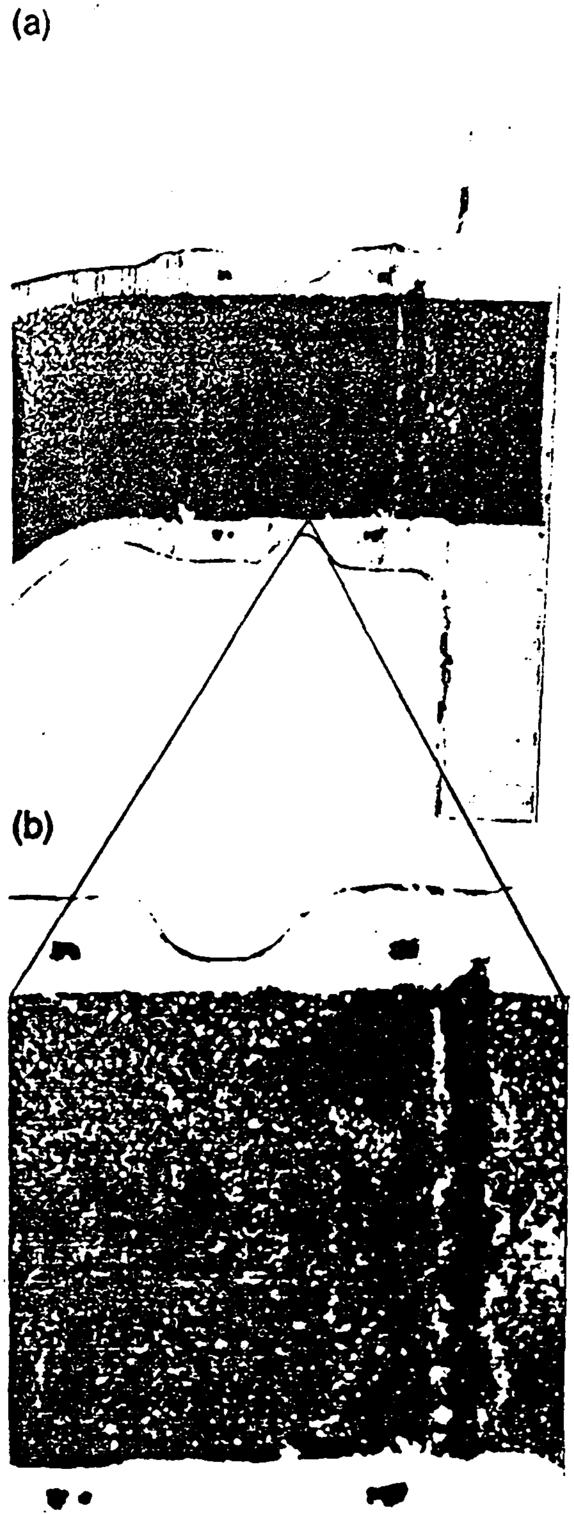
Pre-Reduction Step

$O_2\ (\text{solution}) \rightarrow O_2\ (\text{adsorbed})$

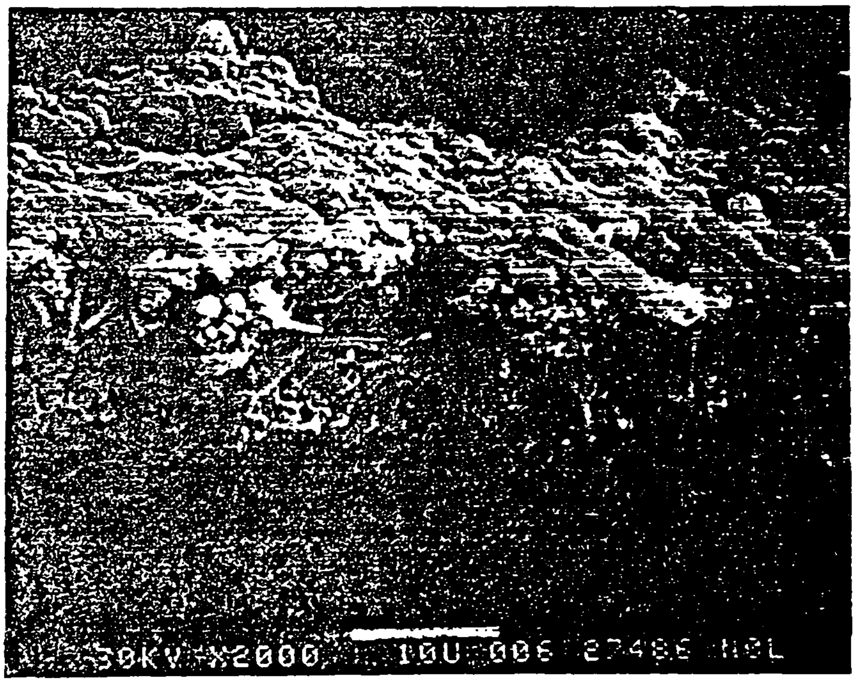
Primary Reduction Reaction

$O_2 + H_2O + 4e^- \rightarrow 4\,OH^-$

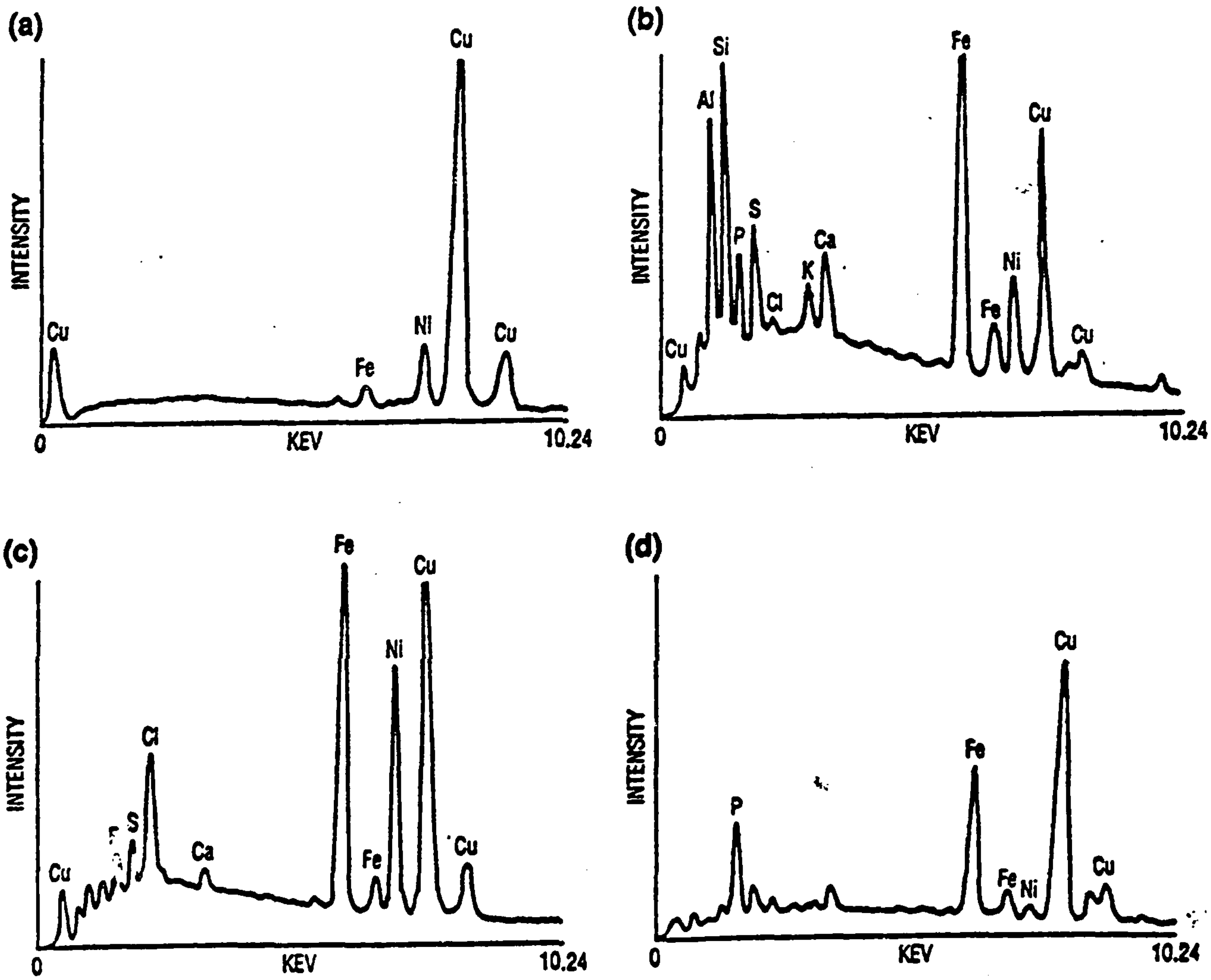
TYPICAL CATHODIC AND ANODIC REACTIONS ON COPPER ALLOYS IN OXYGENATED SEAWATER AND FRESH WATER.



CROSS-SECTION OF 2.5 CM I.D. COPPER ALLOY PIPING AFTER ONE YEAR IN SEAWATER SERVICE, SHOWING THICK SURFACE DEPOSITS AND PITTING.



SCANNING ELECTRON MICROGRAPH OF A CROSS-SECTION OF THE BLACK DEPOSIT WITHIN A PIT OF COPPER ALLOY. BACTERIA ARE WITHIN BLACK DEPOSIT. A SPONGY COPPER-RICH REGION IS BENEATH THE BACTERIA.

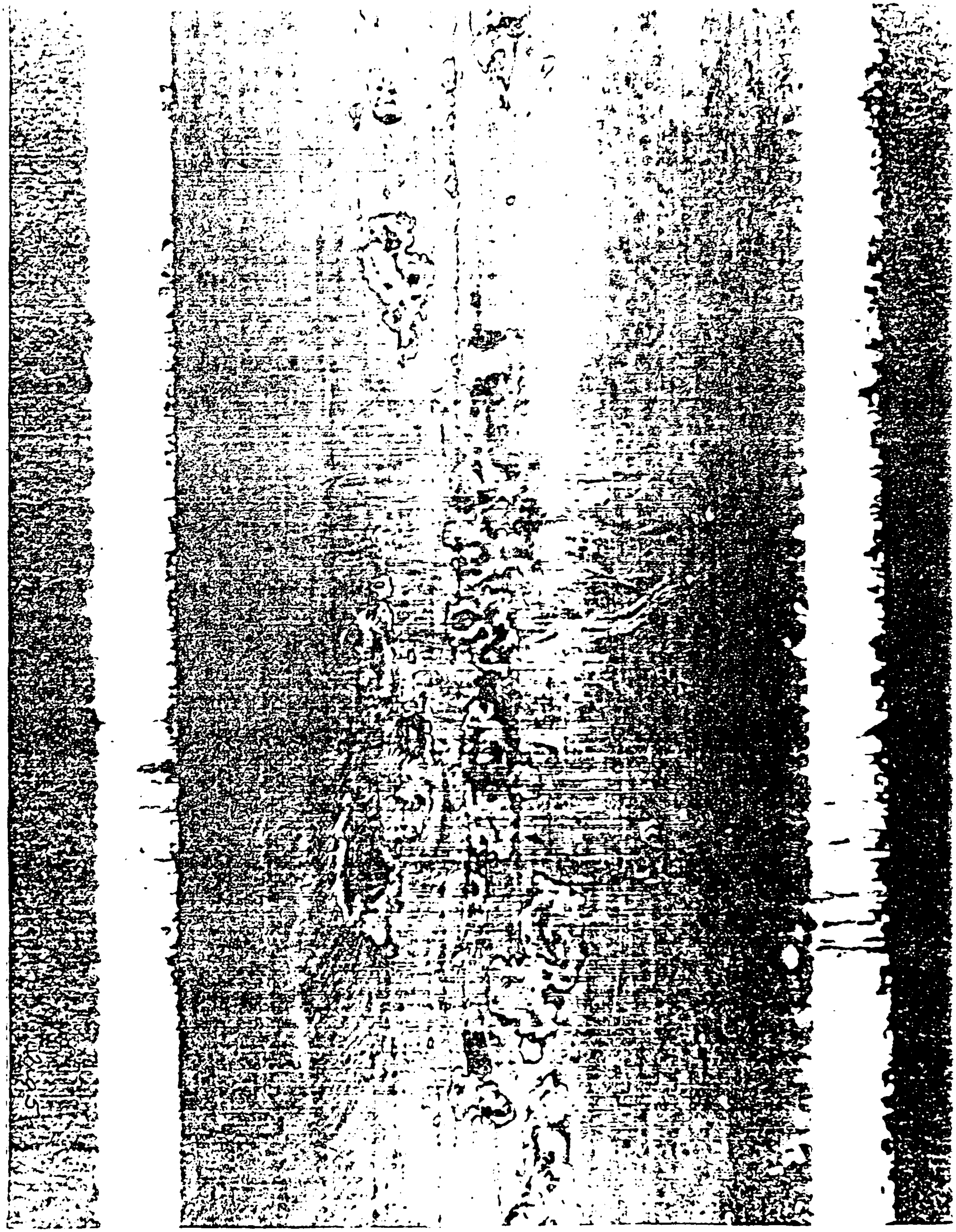


A. EDAX SPECTRUM OF CLEAN COPPER ALLOY BEFORE EXPOSURE

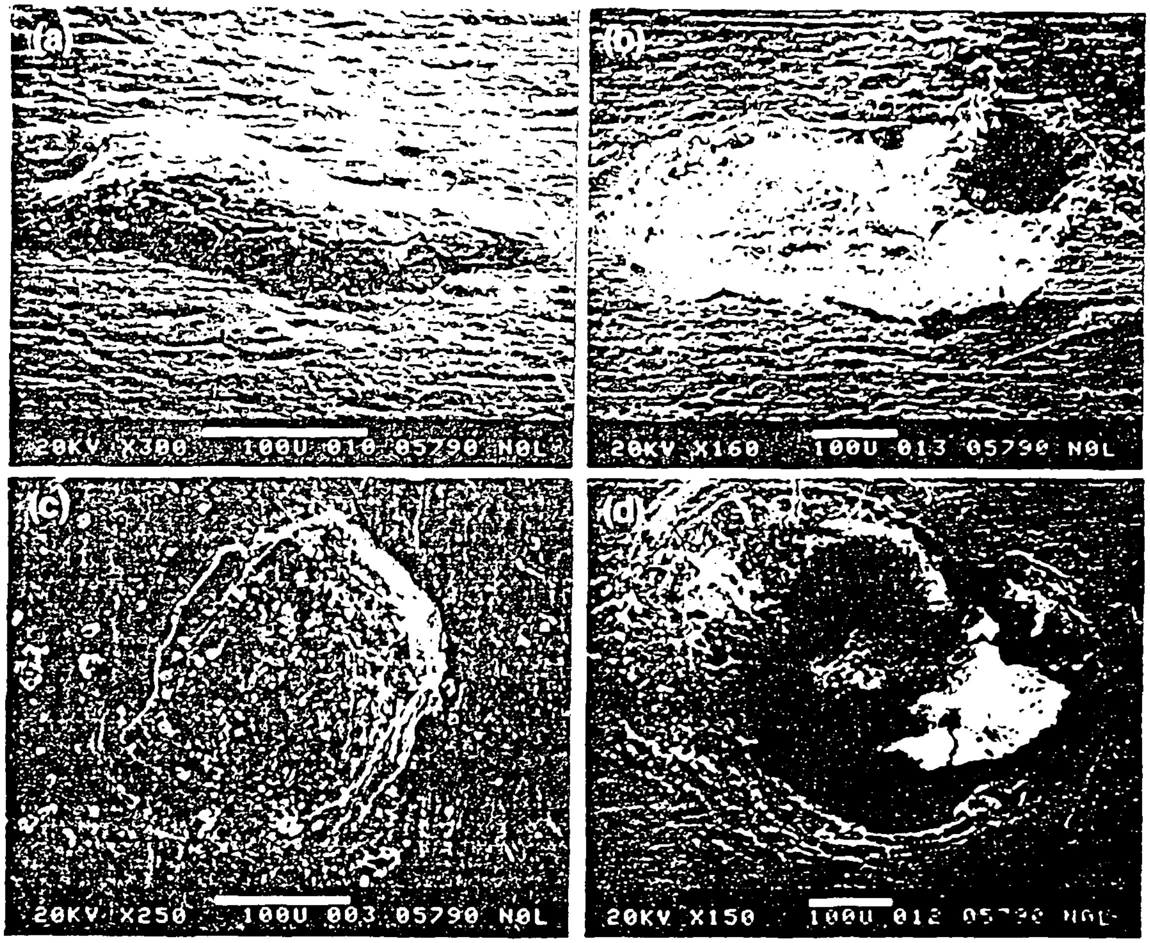
B. EDAX SPECTRUM OF PITTED REGION OF COPPER ALLOY, SHOWING ACCUMULATION OF ALUMINUM, SILICON, PHOSPHORUS, SULFUR, CALCIUM AND ELEVATED AMOUNTS OF IRON AND NICKEL.

C. EDAX SPECTRUM OF PITTED REGION OF COPPER ALLOY, SHOWING THE ACCUMULATION OF CHLORINE AND ELEVATED AMOUNTS OF IRON AND NICKEL.

D. EDAX SPECTRUM OF SPONGY MATERIAL BENEATH BACTERIA, SHOWING AN ACCUMULATION OF PHOSPHORUS, AN ENRICHMENT OF IRON AND A DEPLETION OF NICKEL IN THE BASE OF THE PIT.

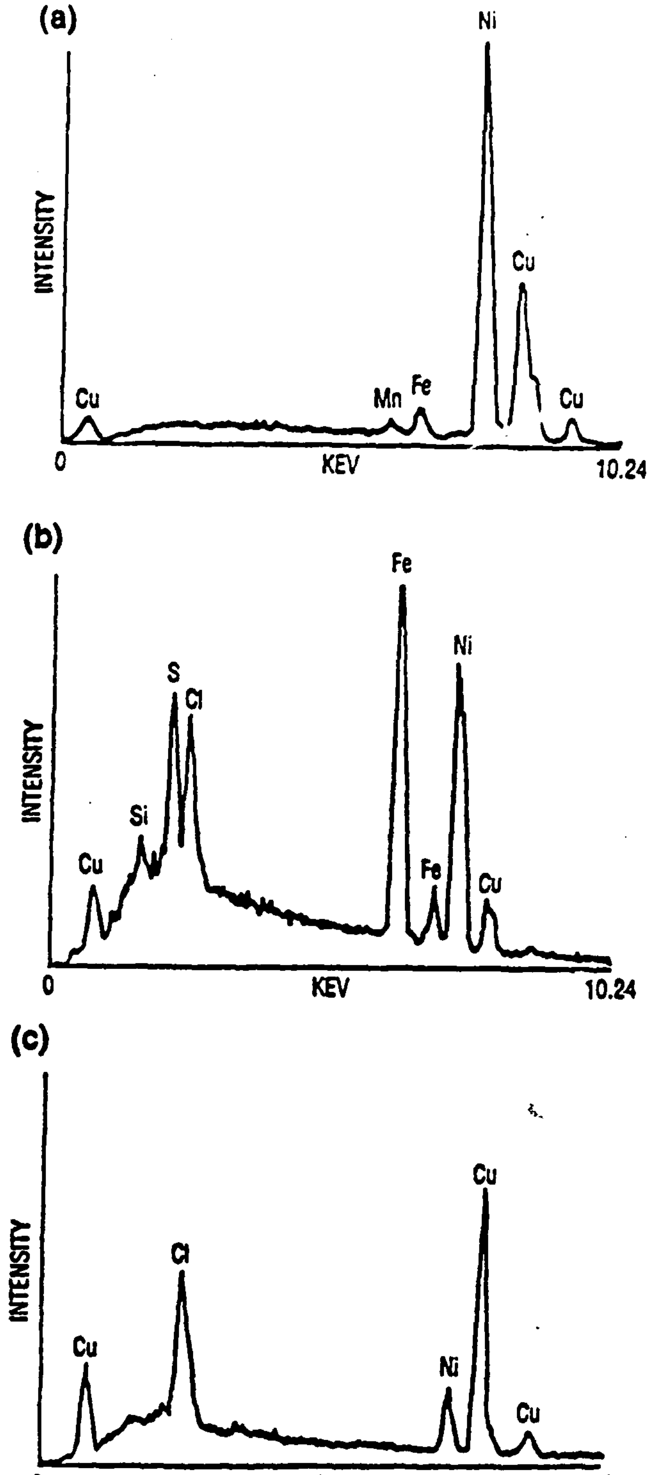


CROSS-SECTION OF 20 MM I.D. NICKEL TUBE AFTER EXPOSURE TO ESTUARINE WATER FOR 6 MONTHS SHOWING SURFACE DEPOSITS AND PITTING.



A AND C. BLISTERS ON THE SURFACE OF NICKEL TUBE.

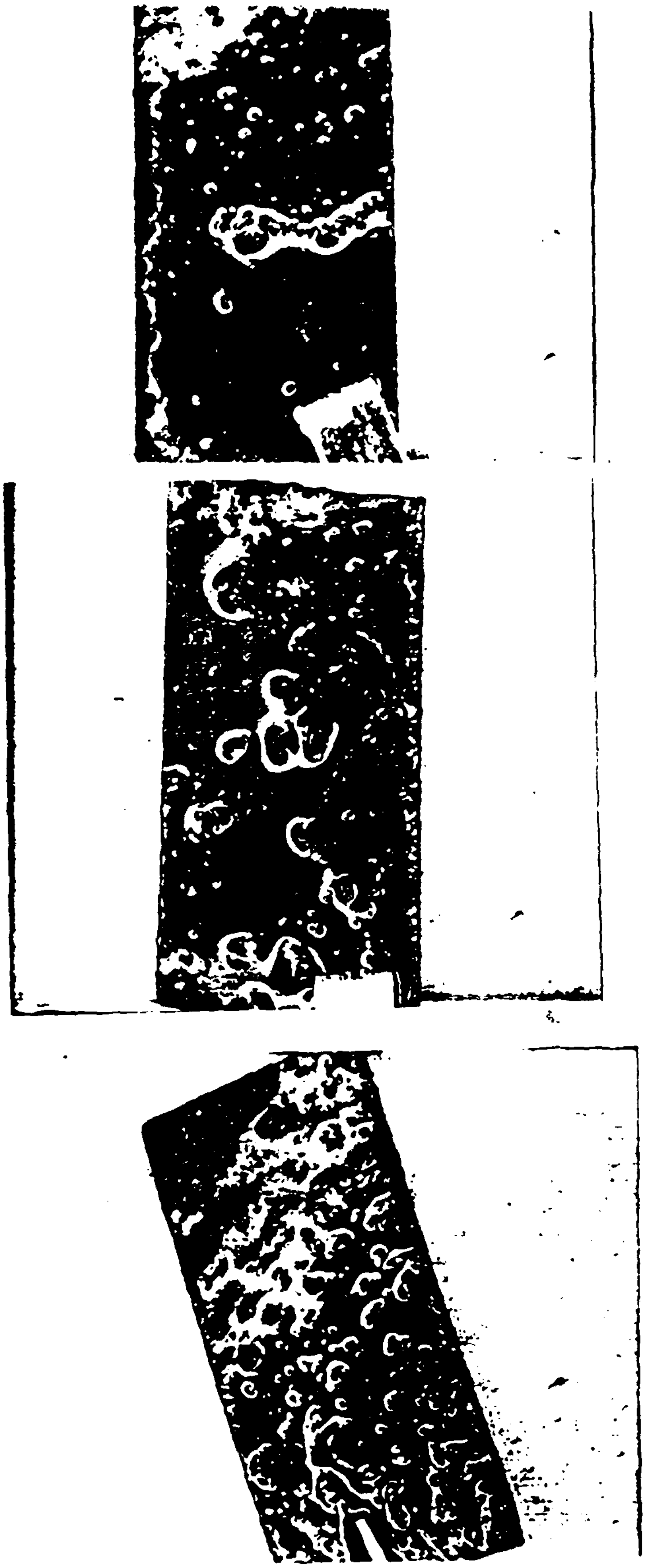
B AND D. PITS ON NICKEL TUBE.



A. EDAX SPECTRUM OF UNEXPOSED NICKEL ALLOY.

B. EDAX SPECTRUM OF NICKEL ALLOY AFTER EXPOSURE TO ESTUARINE WATER FOR 6 MONTHS SHOWING ACCUMULATIONS OF SILICON, SULFUR, AND CHLORINE WITH ELEVATED CONCENTRATIONS OF IRON AND NICKEL.

C. EDAX SPECTRUM OF THE RESIDUAL METAL IN THE BASE OF THE PIT SHOWING NICKEL DEPLETION AND COPPER ENRICHMENT.



DEPOSITS ON 99CU AFTER FOUR MONTHS EXPOSURE TO SRB CULTURES.

SURFACE OF 99CU AFTER FOUR MONTHS EXPOSURE TO CULTURE VI. CORROSION PRODUCTS HAVE SLOUGHED FROM SURFACE REVEALING PITTING.

Minerals in Corrosion Products

	Bacterial Cultures							Augmented Natural Waters		
	I	II	III	IV	V	VI	VII	Gulf of Mexico	Lake Water	Salt Marsh
99Cu		Low-Chalcocite Digenite Djurleite*		Low-Chalcocite Digenite* Anilite		Low Chalcocite High Chalcocite*		Low-Chalcocite	Low-Chalcocite	Low-Chalcocite
90Cu 10Ni		Low Chalcocite High Chalcocite Covellite*		Low Chalcocite High Chalcocite Djurleite*			Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*
70Cu 30Ni						Low Chalcocite Djurleite*	Low Chalcocite Djurleite*			

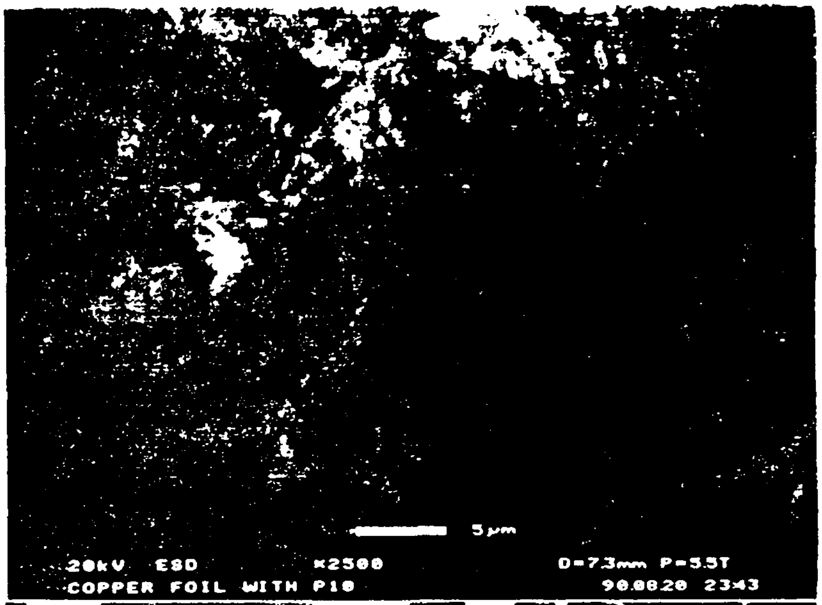
Formulae

Low Chalcocite	Cu_2S
High Chalcocite	Cu_2S
Digenite	Cu_9S_5
Djurleite	$Cu_{1.93}S$-$Cu_{1.97}S$
Anilite	Cu_7S_5
Covellite	CuS

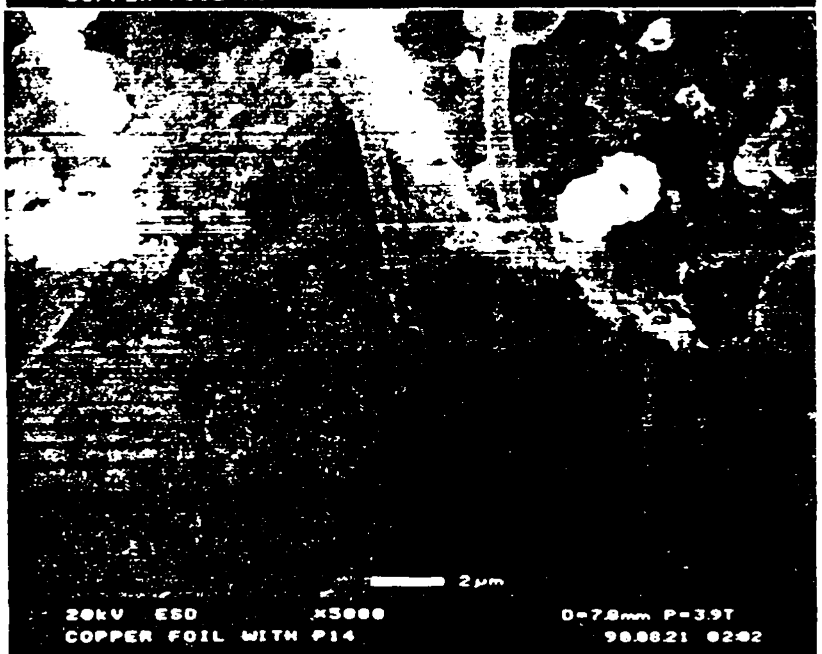
* low concentration

Blanks indicate work that has not been completed

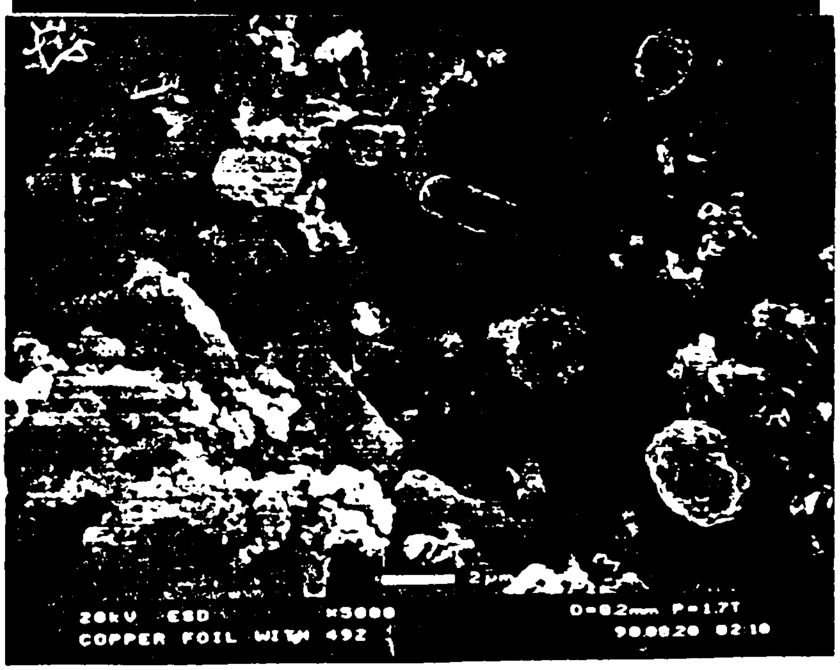
a


5 μm
20kV ESD ×2500 D=7.3mm P=5.5T
COPPER FOIL WITH P10 90.08.20 23:43

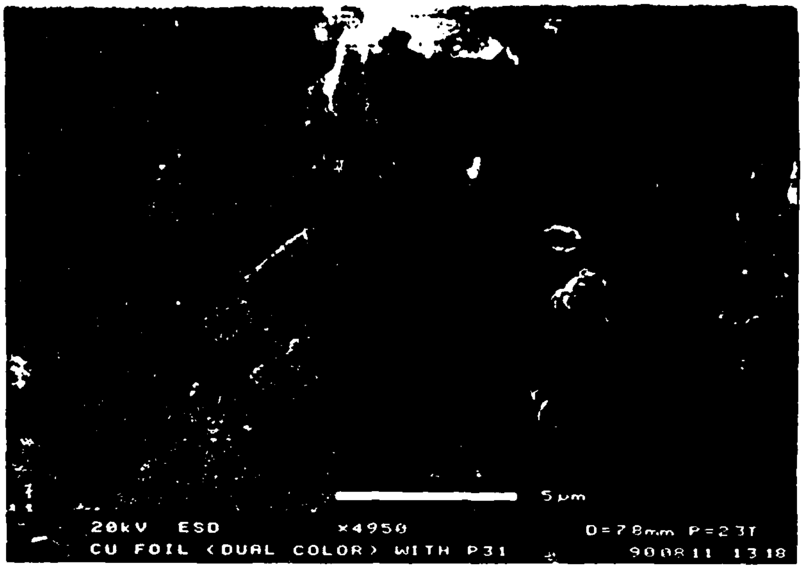
b


2 μm
20kV ESD ×5000 D=7.8mm P=3.9T
COPPER FOIL WITH P14 90.08.21 02:02

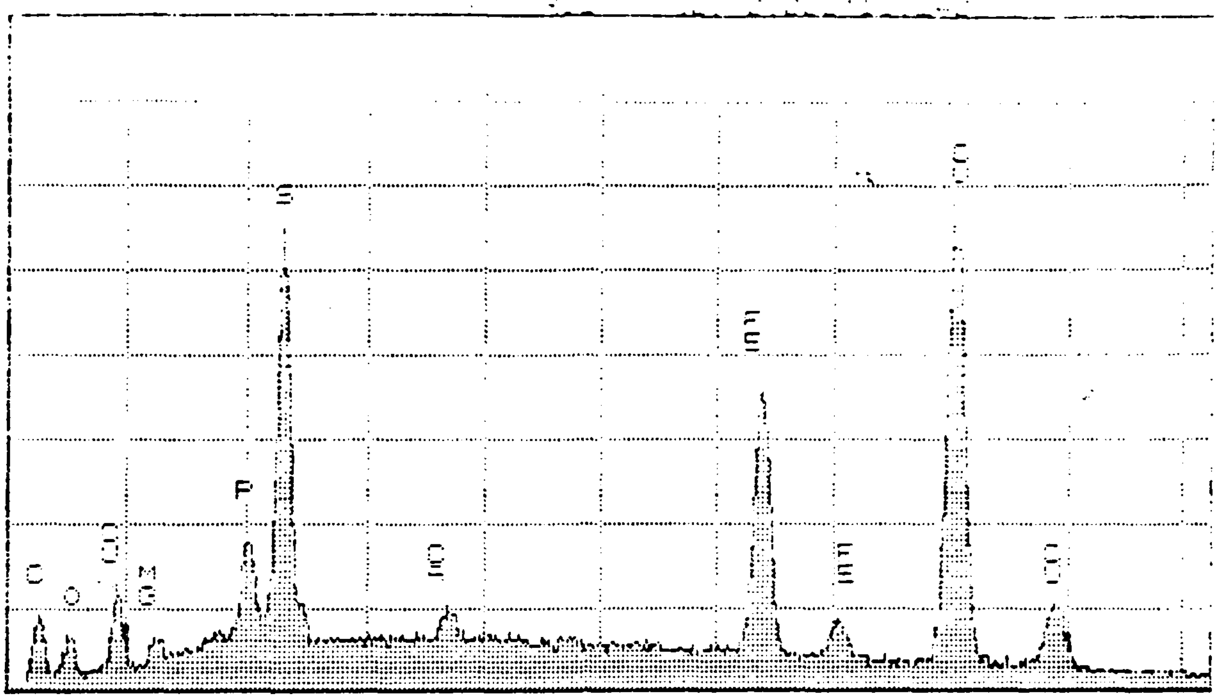
c


2 μm
20kV ESD ×5000
COPPER FOIL WITH 49Z 90.08.20 02:10

d



BACTERIA ASSOCIATED WITH CORROSION PRODUCTS.



0.000 VFS = 1024 10.240

100 COPPER FOIL WITH I14 FLAT TOP LAYER

SQ: QUANTIFY

OPPER FOIL WITH I14 FLAT TOP LAYER
Standardless Analysis
20.0 KV 62.0 Degrees

Chi-sqd = 1.02

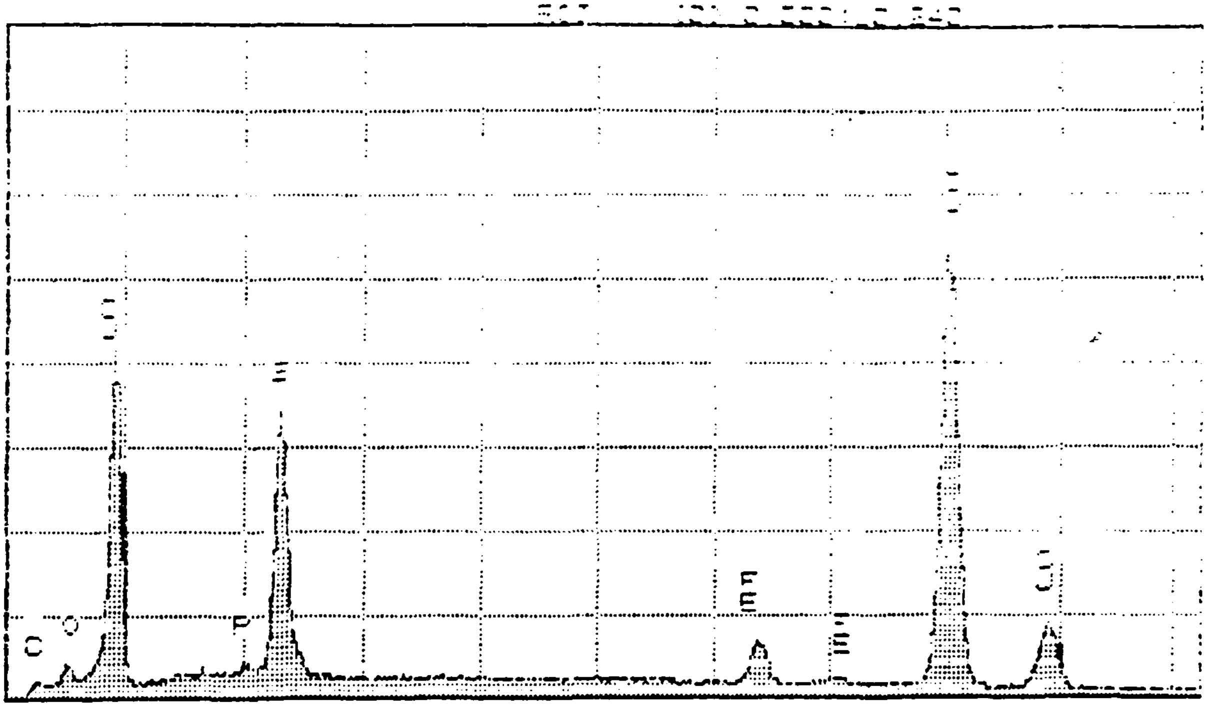
Element	Rel. K-ratio	Net Counts
Cu-L	0.01801 +/- 0.00113	1214 +/- 76
Mg-K	0.00345 +/- 0.00093	333 +/- 90
P -K	0.02056 +/- 0.00203	2204 +/- 218
S -K	0.09776 +/- 0.00284	9663 +/- 281
Ca-K	0.01003 +/- 0.00198	822 +/- 162
Fe-K	0.19403 +/- 0.00568	7521 +/- 220
Cu-K	0.65616 +/- 0.01292	14625 +/- 286

ZAF Correction 20.00 kV 61.96 deg
No.of Iterations = 3

Element	K-ratio	Z	A	F	Atom%	Wt%
Mg-K	0.003	0.909	3.484	0.999	2.31	1.05
P -K	0.020	0.938	1.586	0.994	5.03	2.93
S -K	0.094	0.913	1.407	0.998	20.06	12.10
Ca-K	0.010	0.919	1.109	0.985	1.29	0.97
Fe-K	0.187	1.002	1.011	0.884	15.95	16.76
Cu-K	0.633	1.031	1.014	1.000	55.37	66.18
					Total=	100.00%

EDAX SPECTRUM OF 99CU COLONIZED BY CULTURE IV.

University of Southern [illegible]   [illegible] 02:48
Cursor: 0.000keV = 0   ROI (2) 0.000: 0.000



0.000   VFS = 2048   10.240
100   COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER

Q: QUANTIFY

COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER
Standardless Analysis
20.0 KV   62.0 Degrees

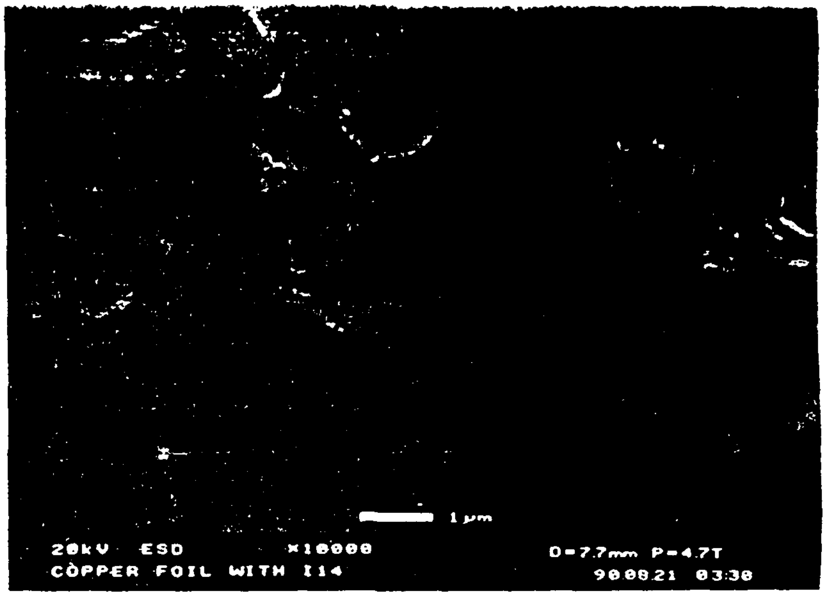
Chi-sqd = 1.16

Element	Rel. K-ratio	Net Counts
Cu-L	0.09590 +/- 0.00160	10367 +/- 173
P -K	0.00259 +/- 0.00111	446 +/- 190
S -K	0.07937 +/- 0.00179	12581 +/- 283
Fe-K	0.04034 +/- 0.00261	2508 +/- [illegible]2
Cu-K	0.78179 +/- 0.00968	27941 +/- 346

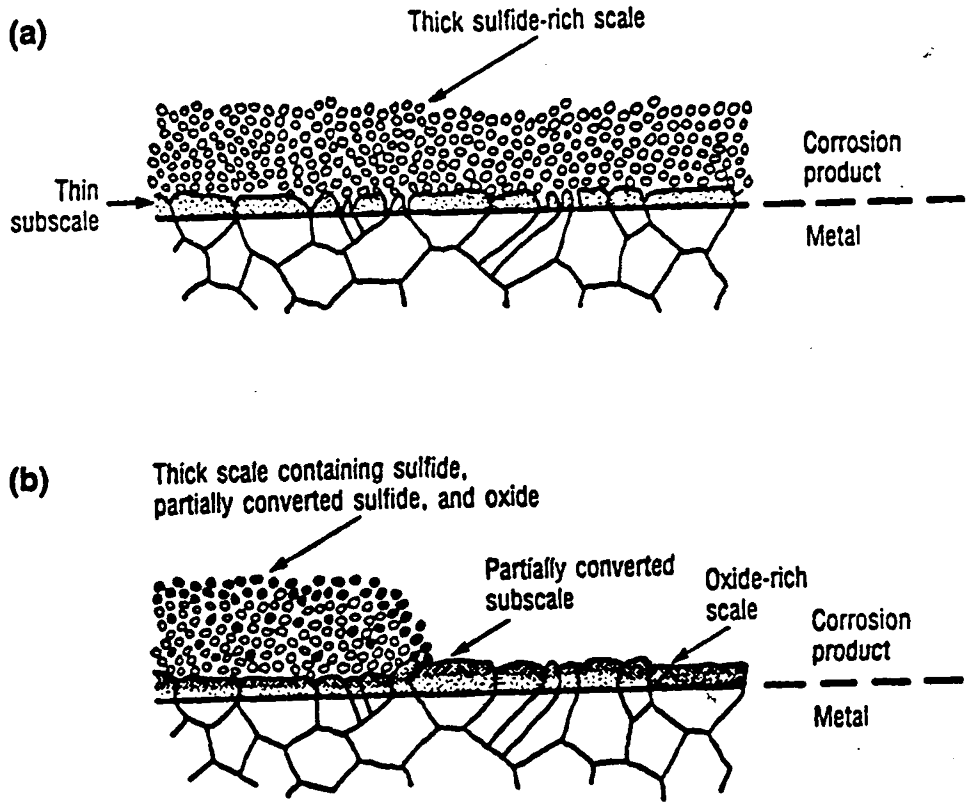
ZAF Correction 20.00 kV 51.95 deg
No.of Iterations = 3

Element	K-ratio	Z	A	F	Atom%	Wt%
P -K	0.003	0.929	1.650	0.995	0.77	[illegible]
S -K	0.085	0.905	1.430	1.799	19.38	10.51
Fe-K	0.043	0.991	1.011	0.318	3.59	3.52
Cu-K	0.832	1.019	1.004	1.000	76.26	85.14
					Total=	100.00%

EDAX SPECTRUM OF THE 99CU METAL SURFACE UNDER CULTURE IV.



ENCRUSTATIONS OF COPPER SULFIDE ALONG BACTERIAL CELL.



A. SCHEMATIC OF THICK SULFIDE-RICH SCALE FORMING ON COPPER ALLOY (TAKEN FROM SYRETT, 1980).

B. SCHEMATIC SHOWING DISRUPTION OF SULFIDE-RICH FILM ON COPPER ALLOY BY THE INTRODUCTION OF AERATED SEAWATER (TAKEN FROM SYRETT, 1980).